Supporting Information

Direct regeneration of fluorine-doped carbon-coated $LiFePO_4$ cathode material from spent lithium-ion battery

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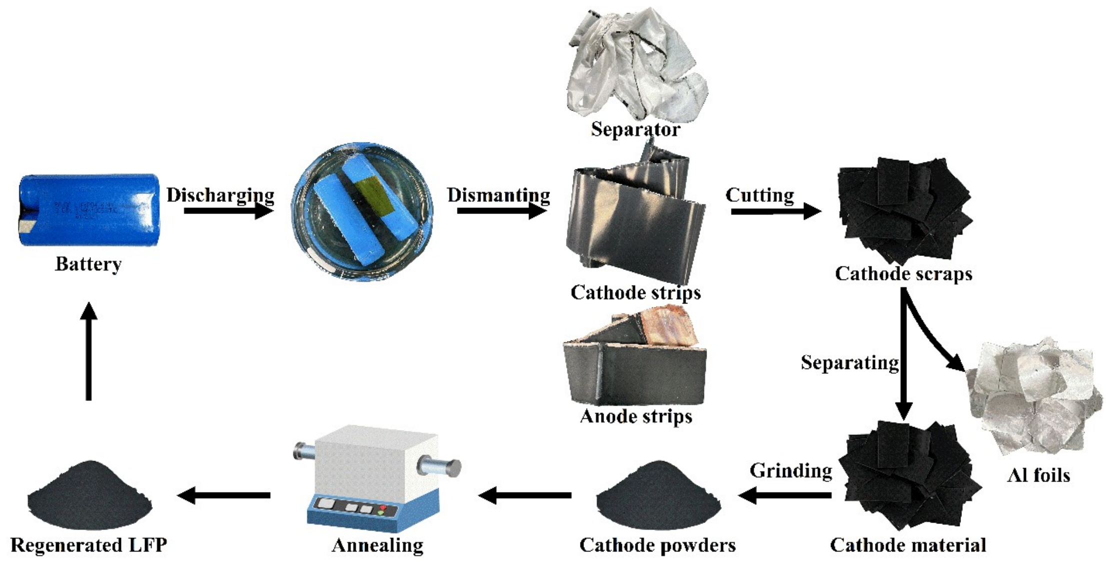


Fig. S1 Flowchart for recycling spent $LiFePO_4$ cathode.

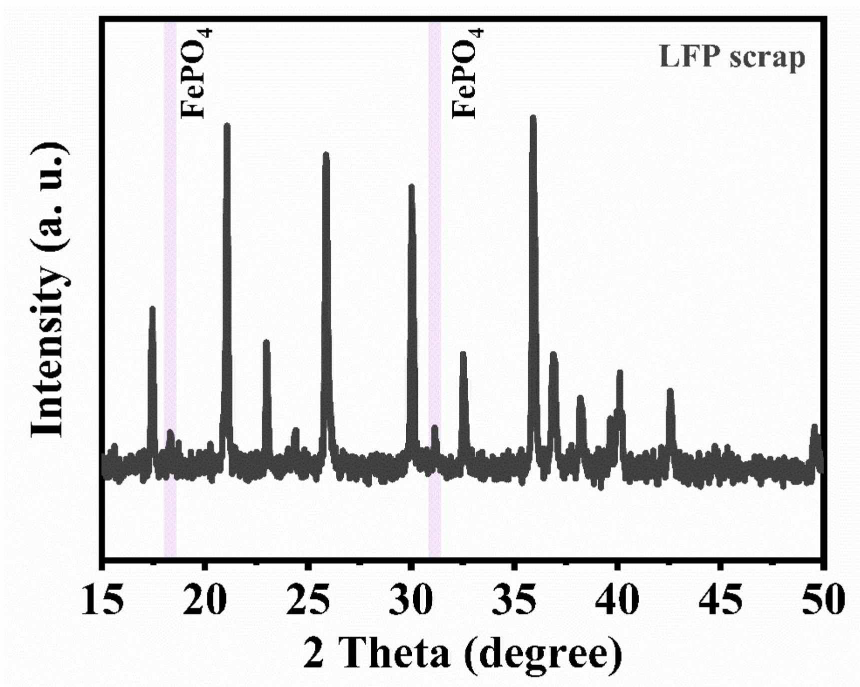


Fig. S2 XRD patterns of LFP scrap.

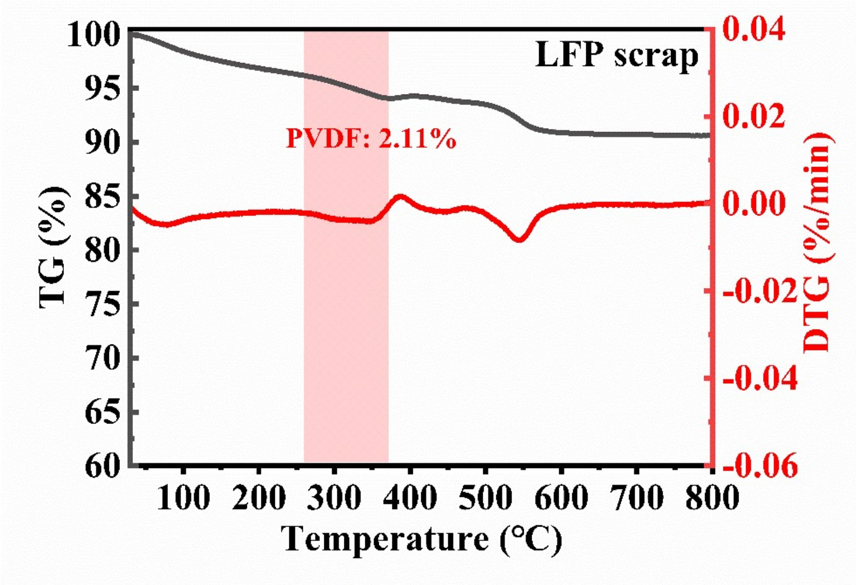


Fig. S3 Thermogravimetric analysis for LFP scrap.

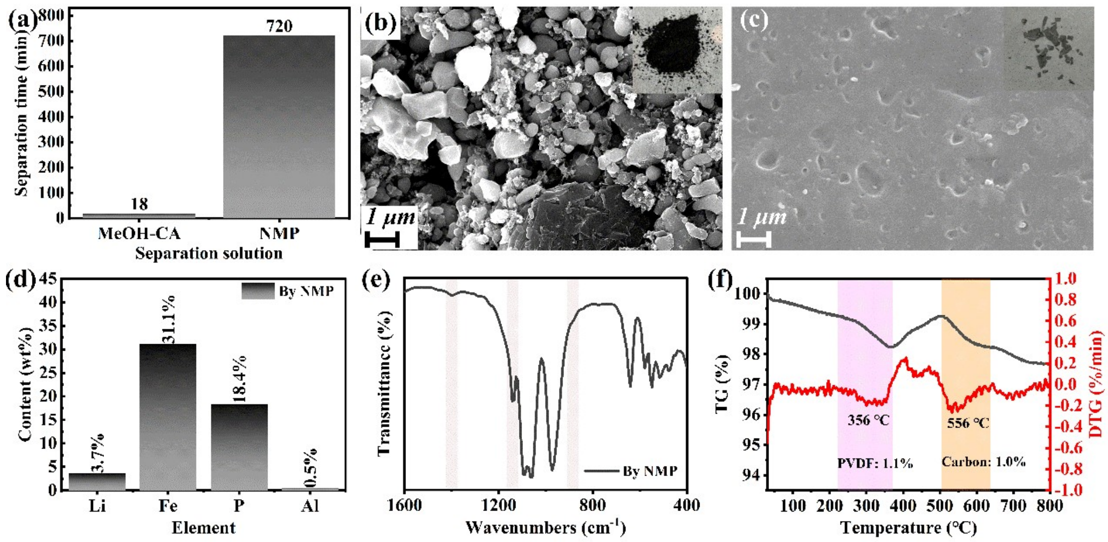


Fig. S4 (a) Comparison of separation time by MeOH-CA and NMP. SEM and digital images of (b) separated LFP and (c) Al foil by NMP solution. (d) Mass contents of Li, Fe, P and Al elements, (e) FTIR spectra and (f) TG and DTG curves of separated LFP by NMP.

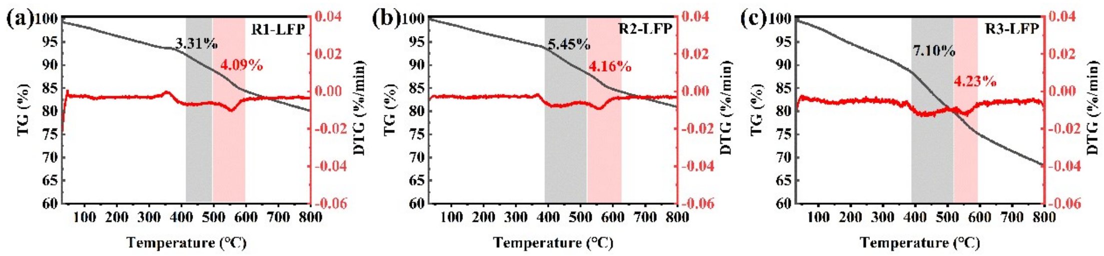


Fig. S5 Thermogravimetric analysis for R1-LFP, R2-LFP and R3-LFP.

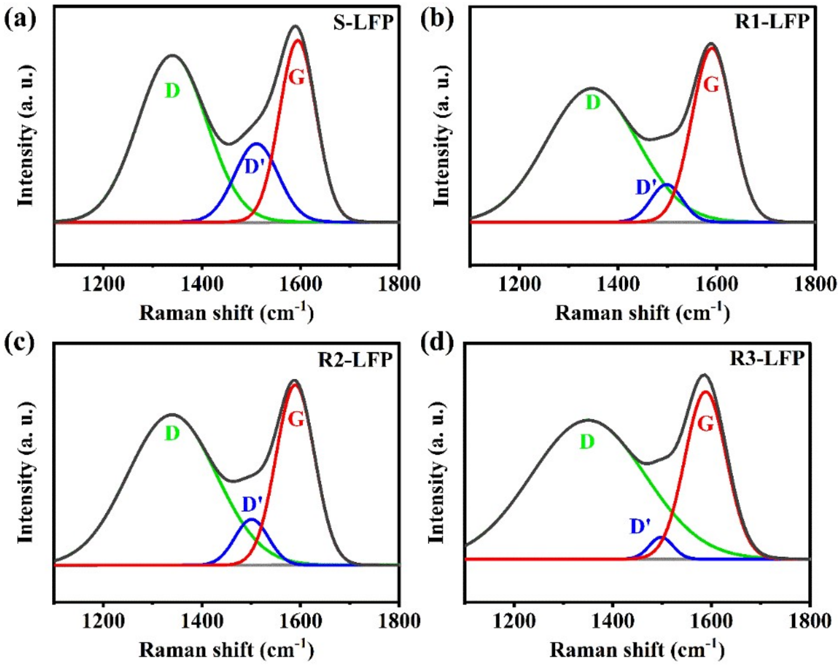
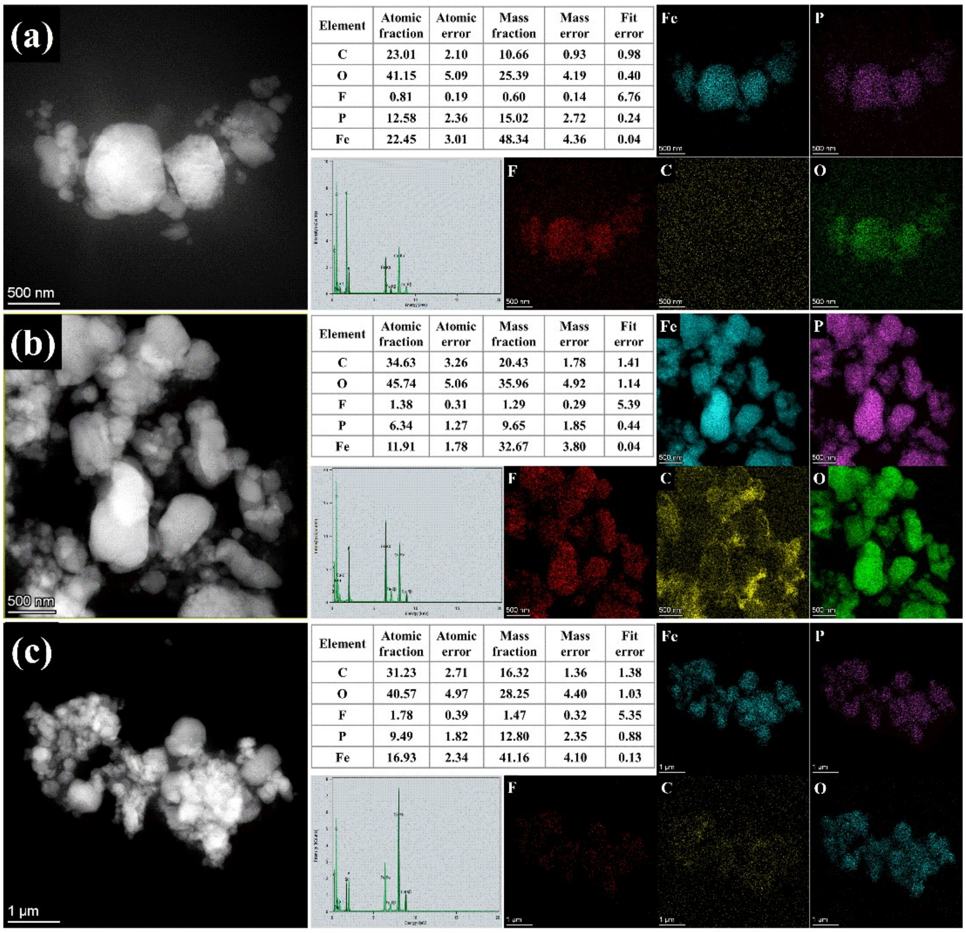


Fig. S6 Fitted Raman spectra of (a) S-LFP, (b) R1-LFP, (c) R2-LFP and (d) R3-LFP. (Raman results were fitted according to the literatures[1].)



(a)

Element	Atomic fraction	Atomic error	Mass fraction	Mass error	Fit error
C	23.01	2.10	10.66	0.93	0.98
O	41.15	5.09	25.39	4.19	0.40
F	0.81	0.19	0.60	0.14	6.76
P	12.58	2.36	15.02	2.72	0.24
Fe	22.45	3.01	48.34	4.36	0.04

(b)

Element	Atomic fraction	Atomic error	Mass fraction	Mass error	Fit error
C	34.63	3.26	20.43	1.78	1.41
O	45.74	5.06	35.96	4.92	1.14
F	1.38	0.31	1.29	0.29	5.39
P	6.34	1.27	9.65	1.85	0.44
Fe	11.91	1.78	32.67	3.80	0.04

(c)

Element	Atomic fraction	Atomic error	Mass fraction	Mass error	Fit error
C	31.23	2.71	16.32	1.36	1.38
O	40.57	4.97	28.25	4.40	1.03
F	1.78	0.39	1.47	0.32	5.35
P	9.49	1.82	12.80	2.35	0.88
Fe	16.93	2.34	41.16	4.10	0.13

Fig. S7 HAADF image, element mapping images and EDS image of (a) R1-LFP, (b) R2-LFP and (c) R3-LFP.

Table S1 Element content and molar ratio of LFP scrap, S-LFP, R1-LFP, R2-LFP and R3-LFP according to ICP-MS results.

	Element content (wt%)				Molar ratio	
	Li	P	Fe	Al	Li/P	Li/Fe
LFP scrap	3.21	16.33	26.68	10.61	0.88	0.97
S-LFP	3.59	18.27	29.84	/	0.88	0.97
R1-LFP	4.01	18.21	29.72	/	0.99	1.08
R2-LFP	4.11	18.17	29.68	/	1.01	1.09
R3-LFP	4.20	18.12	29.65	/	1.02	1.10

Table S2 The results of R_{ct} fitted by EIS for the samples.

	R1-LFP	R2-LFP	R3-LFP	S-LFP
R_{ct} (ohm)	55.19	46.09	54.96	68.08

Table S3 The results of Li^+ diffusion fitted by EIS for the samples.

	R1-LFP	R2-LFP	R3-LFP	S-LFP
Equation	y = a + bx			
Intercept (a)	70.30661 ± 0.13570	51.59065 ± 0.05857	59.72192 ± 0.01595	60.12832 ± 0.42547
Slope (b)	90.03374 ± 0.99842	46.36614 ± 0.43093	70.61076 ± 0.11735	138.55402 ± 3.13046
R-square	0.99939	0.99965	0.99999	0.99796
D_{Li} ($cm^2\ s^{-1}$)	6.58844×10^{-15}	2.48423×10^{-14}	1.07115×10^{-14}	2.78199×10^{-15}

Table S4 Summarized cost of direct recycling 1 t spent LFP scraps via in this study.

Material & Process	Cost ($)	Notes and References
Cathode scrap	2224.41	
Methanol	577.19	
CA·H2O	479.81	
Separating	0.43	Assumed stirred by a 200 L V-shape barrel industrial mixer for 20 runs (20 * 2000 W * 15 min = 480 kW h) and briefly dried in 60°C oven (~7kWh).
Li_2CO_3	226.16	
PVDF	1.56	
Mixing	0.25	Assumed stirred by a 200 L V-shape barrel industrial mixer for 10 runs (10 * 2000 W*0.5 h = 10 kW h)
Annealing	187.80	Based on the analogical energy cost of LFP synthesis[2].
Protective Gas (N_2)	49.46	4 h * 3600 * 2 mL s^{-1} + 40 L per 500 g
Tail gas treatment	5.38	Estimated CO_2 of decomposing all carbonous material.
Others	32.26	Analogical estimation of Ref.[3]
Total ($)	3784.71	

Note: 1 $ = 7.2268 ¥ (Update time: 2024/3/28

Table S5 Summarized cost of direct recycling 1 t spent LFP scraps via traditional method.

Material & Process	Cost ($)	Notes and References
Cathode scrap	2224.41	
NMP	3451.9	
Separating	12.50	Assumed stirred by a 200 L V-shape barrel industrial mixer for 20 runs (20 * 2000 W *12 h = 480 kW h) and briefly dried in 60°C oven (~14 kW h).
Li_2CO_3	226.16	
Glucose	0.03	
Mixing	0.25	Assumed stirred by a 200 LV-shape barrel industrial mixer for 10 runs (10 * 2000 W * 0.5 h = 10 kW h)
Annealing	187.80	Based on the analogical energy cost of LFP synthesis[2].
Protective Gas (N_2)	49.46	4 h * 3600 * 2 mL s^{-1} + 40 L per 500 g
Tail gas treatment	5.38	Estimated CO_2 of decomposing all carbonous material.
Others	32.26	Analogical estimation of Ref.[3]
Total ($)	6190.15	

Note: 1 $ = 7.2268 ¥ (Update time: 2024/3/28

Table S6 The benefits of direct recycling 1 t spent LFP scraps.

		Traditional method		This study	
	Price ($/t)	Dosage (t)	Benefit ($)	Dosage (t)	Benefit ($)
R-LFP	6005.42	0.84	-1145.60	0.84	1259.84
Conductive carbon	1695.13	/	/	0.02	33.91
Total ($)			-1145.60		1293.75

Table S7 The summary of several direct recycling processes for spent LFP cathode material in recent years.

Reagents	**Mixture compositions**	**Optimized conditions (T, t)**	**Annealing parameters**	**Regenerated capacity**
LiOH and citric acid[4]	LFP with 80 mL of 0.2 M LiOH and 0.08 M citric acid solutions; excess 4% Li_2CO_3.	180 °C, 5 h	600 °C, 2 h in N_2	159 mAh g^{-1} (0.5 C, 2.5-3.8 V)
Li_2SO_4 and $N_2H_4·H_2O$[5]	5 g of LFP with 30 mL of Li_2SO_4 solution, and 1.0 mL of $N_2H_4·H_2O$	200 °C, 3 h	/	141.9 mAh g^{-1} (1 C, 2.2-4.2 V)
LiOH and L-ascorbic acid[6]	Molar ratio of LFP:LiOH:L-ascorbic acid is 1:3:3	160 °C, 6 h	/	162.8 mAh g^{-1} (0.2 C, 2.5-4.2 V)
CH_3COOLi and L-threonine[7]	1 g of LFP with 180 g of CH_3COOLi and 180 g of L-threonine	180 °C, 6 h	/	147.9 mAh g^{-1} (1 C, 2.5-4.3 V)
Polycyclic aryl-lithium compound[8]	0.5 g of LFP with 5.6 mL 0.2M of polycyclic aryl-lithium compound	80 °C, 15 min in Ar glovebox	/	138 mAh g^{-1} (0.5 C, 2.8-4.2 V)
LiI and ethanol[9]	1 g of LFP with 266.4 mg of LiI and 50 mL of ethanol	Ambient, 24 h	/	166 mAh g^{-1} (1 C, 2.1-4.2 V)
LiOH and H_2O_2[10]	A solid–liquid ratio of 5 g L^{-1} of LFP, 3 vol% dosage of H_2O_2 and 0.05 M of LiOH solution; excess 3% Li_2CO_3.	30 °C, 1 h	700 °C, 2 h in N_2	141.4 mAh g^{-1} (1 C, 2.5-4.3 V)
Li_2CO_3[11]	Excess 3% Li_2CO_3	/	650 °C, 1 h in Ar/H_2	140.4 mAh g^{-1} (0.5 C, 2.5-4.2 V)
Li_2CO_3 and glucoses[12]	Excess 3% Li_2CO_3, 12 wt % glucose	/	550 °C, 2 h in N_2; 700 °C, 10 h in N_2	122.6 mAh g^{-1} (0.5 C, 2.5-3.8 V)
Li_2CO_3 and glucoses[13]	Excess 3% Li_2CO_3, 12 wt % glucose	/	550 °C, 2 h in air; 700 °C, 10 h in N_2	155.7 mAh g^{-1} (0.5 C, 2.5-3.8 V)
3,4-dihydroxybenzonitrile dilithium[14]	/	/	800 °C, 6 h in Ar/H_2	146 mAh g^{-1} (1 C, 2.5-4.3 V)
$LiNO_3$ and anhydrous glucose[2]	1 g of LFP with 0.8 g of $LiNO_3$ and 0.02 g of anhydrous glucose	/	300 °C, 0.5 h in air	162 mAh g^{-1} (0.1 C, 2.6-4.2 V)
Li_2CO_3, CNTs and glucose[15]	LFP with 5 wt% of CNTs, 15 wt% of glucose and 5 wt% of Li_2CO_3	/	350 °C, 2h in Ar; 650 °C, 12h in Ar	155.5 mAh g^{-1} (0.05 C, 2.0-3.8 V)
Li_2CO_3 and PVDF[This study]	Excess 5 mol% Li_2CO_3, 5 wt% of PVDF	/	650 °C, 2 h in N_2	159.2 mAh g^{-1} (0.1 C, 2.5-4.2 V)

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